Facile hydrothermal preparation of titanium dioxide decorated reduced graphene oxide nanocomposite

Betty Yea Sze Chang1
Nay Ming Huang1
Mohd Nor An’amt2
Abdul Rahman Marlinda1
Yusoff Norazriena1
Muhamad Rasat Muhamad3
Ian Harrison4
Hong Ngee Lim5
Chin Hua Chia6

1Low Dimensional Materials Research Center, Physics Department, University of Malaya, Kuala Lumpur; 2Faculty of Agro Industry and Natural Resources (FASA), Universiti Malaysia Kelantan, Kota Bharu, Kelantan; 3The Chancellery Building, Multimedia University, Persiaran Multimedia, Cyberjaya, Selangor; 4School of Chemical and Environmental Engineering, The University of Nottingham Malaysia Campus, Semenyih, Selangor; 5Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, Serdang, Selangor; 6School of Applied Physics, Universiti Kebangsaan Malaysia, Bangi, Selangor, Malaysia

Correspondence: NM Huang
Low Dimensional Materials Research Center, Physics Department, University of Malaya, 50603 Kuala Lumpur, Malaysia
Tel +60 3 7967 4295
Fax +60 3 7967 4146
Email huangnayming@gmail.com

Abstract: A simple single-stage approach, based on the hydrothermal technique, has been introduced to synthesize reduced graphene oxide/titanium dioxide nanocomposites. The titanium dioxide nanoparticles are formed at the same time as the graphene oxide is reduced to graphene. The triethanolamine used in the process has two roles. It acts as a reducing agent for the graphene oxide as well as a capping agent, allowing the formation of titanium dioxide nanoparticles with a narrow size distribution (∼20 nm). Transmission electron micrographs show that the nanoparticles are uniformly distributed on the reduced graphene oxide nanosheet. Thermogravimetric analysis shows the nanocomposites have an enhanced thermal stability over the original components. The potential applications for this technology were demonstrated by the use of a reduced graphene oxide/titanium dioxide nanocomposite-modified glassy carbon electrode, which enhanced the electrochemical performance compared to a conventional glassy carbon electrode when interacting with mercury(II) ions in potassium chloride electrolyte.

Keywords: graphene oxide, titanium oxide, hydrothermal, nanocomposite

Introduction

Graphene is a monocrystalline graphitic film a few atoms thick and is stable under ambient conditions. The physical dimension of the film’s thickness ensures the electronic structure of the material is two-dimensional. Moreover, there is a small overlap between the valence and conduction bands, and graphene exhibits semimetal behavior. With the addition of a gate electrode, electron and hole concentrations in the channel can be as high as 10¹³ cm⁻³ with mobility at room temperature in the order of 10,000 cm²V⁻¹ s⁻¹. These results make graphene an ideal candidate for the next generation of electronic devices.¹ In addition, graphene has extremely good mechanical and thermal properties and thus has potential application over a wide variety of uses such as composite materials, fuel cells, batteries, chemical detectors, and solar cells.²–¹¹ Moreover, the integration of graphene with inorganic nanoparticles allows the properties of the nanocomposite to be engineered for specific applications, which is rapidly becoming a research trend as the nanocomposites are able to exhibit properties that are not found in the individual components.⁶,¹₂–¹₈

Nanocrystalline titanium dioxide (TiO₂) is a promising candidate for solar energy conversion applications such as photocatalysis, photochromism, and photovoltaics because of its unique optical and electrical properties.¹⁹ It is widely used in applications such as hydrogen production,²⁰,²¹ gas sensors,²²,²³ photocatalytic activities,²⁴,²⁵ and dye-sensitized solar cells²⁶,²⁷ because of its relative high efficiency and high stability.
The microbiocidal effects of TiO\textsubscript{2} photocatalytic reactions\textsuperscript{28} clearly have pharmacological applications and TiO\textsubscript{2} photocatalytic reactions have been used to kill a wide spectrum of organisms including bacteria,\textsuperscript{29} viruses,\textsuperscript{30} fungi,\textsuperscript{31} cancer cells,\textsuperscript{32} and algal toxins.\textsuperscript{33} In addition, antibacterial activity against four common human pathogens, namely Escherichia coli, Pseudomonas aeruginosa, Klebsiella pneumoniae, and Staphylococcus aureus, has also been demonstrated.\textsuperscript{34} In addition, the oxidizing power of TiO\textsubscript{2} when under irradiation of ultraviolet (UV) light in either water or an oxygen-rich environment means that irradiated TiO\textsubscript{2} can be used in waste processing because of its ability to decompose and/or oxidize most organic and/or inorganic compounds.\textsuperscript{36,37} Interestingly, its high chemical stability and nontoxicity also makes TiO\textsubscript{2} biocompatible, and it is used in many cosmetic products and as an alternative material for improving antimicrobial properties. For example, TiO\textsubscript{2} nanoparticles have been added to dental acrylic resins to improve the color.\textsuperscript{35}

The challenge when developing convenient and effective processing technologies for the fabrication of graphene nanocomposites is the prevention of the restacking and/or agglomeration of the graphene sheets caused by the changes in the Van der Waals interactions due to the presence of metal oxide particles like TiO\textsubscript{2}.\textsuperscript{38,39} Recently, graphene/TiO\textsubscript{2} nanocomposites have been synthesized using technologies such as atomic layer deposition\textsuperscript{40} and electron beam irradiation.\textsuperscript{41} Although successful, these methods are probably not commercially viable since the processes require a six-step sequence with heat treatment at various temperatures\textsuperscript{40} or pretreated graphene\textsuperscript{41} as a raw material. Furthermore, other reported techniques that use hazardous chemicals, such as hydrazine hydrate, create dangerous by-products such as hydrogen fluoride.\textsuperscript{42} Other reported problems in the formation of graphene nanocomposites include the lack of discrete nanocrystalline TiO\textsubscript{2} particles before calcination\textsuperscript{43} and agglomeration of the TiO\textsubscript{2} particles.\textsuperscript{44,45}

In this paper, a one-step hydrothermal route for the preparation of graphene/TiO\textsubscript{2} nanocomposites using graphene oxide (GO) and titanium isopropoxide as starting materials with the addition of triethanolamine (TEA) is reported. The hydrothermal technique was chosen because it is a “soft solution chemical processing” technique, which provides an easier way to control particle size, particle morphology, microstructures, phase composition, and surface chemical properties with adjustments in experimental parameters such as temperature, pressure, duration of process, and pH value of solution.\textsuperscript{46–49} This one-step hydrothermal method is convenient and safe, and with the addition of TEA to the solution, the process provides a route to manufacture graphene/TiO\textsubscript{2} nanocomposites where the TiO\textsubscript{2} nanoparticles are discrete with no agglomeration of the particles. This is not the first time a single-step hydrothermal technique has been reported; however, there are significant differences between the process reported in this paper and those already published. Shen et al reported an “intrinsically pure process,” which utilized only water and glucose.\textsuperscript{50} However, their sample prior to hydrothermal treatment contained ammonium chloride, ethanol, glucose, and ammonium hydroxide.\textsuperscript{50} In the method reported here, only TEA and ethanol were added. Other reported one-step hydrothermal processing studies used ultrasonication to obtain a well-dispersed suspension of GO and TiO\textsubscript{2}. This step was omitted in the current work.

The objective of this work was to study the influence of the hydrothermal temperature on the crystallinity, size distribution, thermal stability, and electrochemical performance of reduced GO (RGO)/TiO\textsubscript{2} nanocomposites. To the best of the authors’ knowledge, the effect of TEA and reaction temperature on the formation of RGO/TiO\textsubscript{2} nanocomposites has not been previously reported.

**Material and methods**

**Materials**

Graphite 3061 and titanium isopropoxide (99%) were purchased from Asbury Graphite Mills Inc (Asbury, NJ) and Acros Organics (Geel, Belgium), respectively; TEA and potassium permanganate were obtained from R&M Chemicals (Systerm, Malaysia). The other materials—sulfuric acid, phosphoric acid, hydrogen peroxide, and ethanol—were purchased from Merck KGaA (Darmstadt, Germany). Unless otherwise specified, all the reagents and materials involved were used as received without further purification. Deionized water (resistivity $\geq 18$ M$\Omega$) was used during the experimental process.

**Synthesis of GO**

GO was synthesized via the simplified Hummers method in which a 9:1 sulfuric acid:phosphoric acid (360:40 mL) solution was prepared, into which 3 g of graphite was added.\textsuperscript{31,52} Potassium permanganate (18 g) was gradually added and the solution was left to oxidize for 3 days whilst being continuously stirred. After 3 days, the resulting solution was cooled to room temperature and poured onto ice (400 mL) along with 27 mL of 30% hydrogen peroxide. The solution was centrifuged (CR21GIII; Hitachi, Japan) and washed three times with 1 M hydrogen chloride and six times with water. The final solution, the GO dispersion, was light brown in color.
Synthesis of RGO/TiO$_2$

Titanium isopropoxide (3.72 mL) was added into 3.32 mL of TEA in a 25 mL volumetric flask (Favorit, PLT Scientific Sdn. Bhd) producing a titanium(IV) ionic (Ti$^{4+}$) solution with a concentration of 0.50 M. In order to form the GO/TiO$_2$ solution, 10 mL of 1 mg/mL of GO solution was added into a water:ethanol mixture (1:14) mL with continuous stirring. After that, 3 mL of Ti$^{4+}$ solution was added and the mixture stirred for 24 hours at room temperature to obtain a homogeneous suspension. The mixture was placed in a custom made Teflon-lined autoclave and heated to 120°C for 24 hours. Two other samples were prepared by an identical procedure except for the final autoclave reaction temperature (150°C and 180°C). The samples were labeled as 120 RGO/TiO$_2$, 150 RGO/TiO$_2$, and 180 RGO/TiO$_2$, with the number signifying the reaction temperature. The black precipitates were washed three times with ethanol, centrifuged at 13,000 g for 10 minutes, and dried at 60°C. Pure TiO$_2$ samples were also prepared using the same procedure; these samples are denoted as 120TiO$_2$, 150TiO$_2$, and 180TiO$_2$. RGO was also synthesized in the absence of titanium isopropoxide under the same conditions at 180°C.

Characterization

The atomic structure of the samples was investigated by X-ray diffraction (XRD, D5000, Siemen) (XRD) using copper K$\alpha$ radiation ($\lambda = 1.5418$ Å) at a scan rate of 0.02 degrees s$^{-1}$. This was complemented by transmission electron microscopy (CM12; Philips) operated at 100 kV, which allowed an image of the nanoparticles and graphene flakes to be acquired. The chemical stability was investigated using thermogravimetric analysis (TGA) (Q500; TA Instruments, New Castle, DE) and the bond structure investigated using UV-visible spectroscopy with a scan rate of 240 nm/mm (Evolution 300; Thermo Fisher Scientific, Pittsburgh, PA). The electrochemical performance was assessed using three-electrode cyclic voltammetry with a scan rate of 240 nm/mm (Evolution 300; Thermo Fisher Scientific, Pittsburgh, PA). The electrochemical performance of the samples as a result of the hydrothermal and chemical reduction process. All the RGO/TiO$_2$ nanocomposites are shown in Figure 1 and indicate the degree of reduction in the increase of GO as the reaction temperature increased. For pure GO, there was a peak at about 227 nm and a shoulder at around 300 nm. The peak at 227 nm is assigned to the pi to anti-pi ($\pi \rightarrow \pi^*$) transition of the aromatic carbon–carbon bonds and the shoulder at 300 nm to the n to anti-pi (n $\rightarrow \pi^*$) transitions of the carbon = oxygen bonds.$^{34}$ The 120 RGO/TiO$_2$ sample had a broad peak centered at 227 nm and a shoulder at approximately 300 nm. There was no evidence of a peak at 256 nm, which is a characteristic of graphene and is attributed to the aromatic carbon = carbon bonds. For the 150 RGO/TiO$_2$ and 180 RGO/TiO$_2$ samples, the peak at 227 nm right-shifted to 256 nm. This represents the partial restoration of the pi-conjugation network of the sample as a result of the hydrothermal and chemical reduction process. All the RGO/TiO$_2$ nanocomposite samples showed typical absorption of TiO$_2$ with an absorption edge of around 256 nm.

Results and discussion

UV-visible absorption spectroscopy measurements for RGO/TiO$_2$ nanocomposites are shown in Figure 1 and indicate the degree of reduction in the increase of GO as the reaction temperature increased. For pure GO, there was a peak at about 227 nm and a shoulder at around 300 nm. The peak at 227 nm is assigned to the pi to anti-pi ($\pi \rightarrow \pi^*$) transition of the aromatic carbon–carbon bonds and the shoulder at 300 nm to the n to anti-pi (n $\rightarrow \pi^*$) transitions of the carbon = oxygen bonds.$^{34}$ The 120 RGO/TiO$_2$ sample had a broad peak centered at 227 nm and a shoulder at approximately 300 nm. There was no evidence of a peak at 256 nm, which is a characteristic of graphene and is attributed to the aromatic carbon = carbon bonds. For the 150 RGO/TiO$_2$ and 180 RGO/TiO$_2$ samples, the peak at 227 nm right-shifted to 256 nm. This represents the partial restoration of the pi-conjugation network of the sample as a result of the hydrothermal and chemical reduction process. All the RGO/TiO$_2$ nanocomposite samples showed typical absorption of TiO$_2$ with an absorption edge of around 256 nm.
In addition to the peaks attributable to carbon-based compounds, the XRD spectrum contained peaks which have been assigned to reflections from the anatase phase of tetragonal TiO$_2$ with lattice constants of $a = 3.7892$ Å, $b = 3.7892$ Å, $c = 9.5370$ Å, and $\beta = 90.0000$ (ICPDS 71-1167). The diffraction peaks can be indexed as reflections from the (101), (004), (200), (105), (211), and (204) planes, respectively. There was no evidence for the other phases of TiO$_2$ being present. Comparing the 120 RGO/TiO$_2$ and the 180 RGO/TiO$_2$ samples, there was an increase in peak intensities of the peaks attributed to the reflections from TiO$_2$, which suggests the formation of larger TiO$_2$ crystallites and enhancement of the TiO$_2$ crystallization process. The full width at half maximum of the TiO$_2$ (101) reflection for the 120 RGO/TiO$_2$, 150 RGO/TiO$_2$, and 180 RGO/TiO$_2$ samples was 1.1595 degrees, 0.9832 degrees, and 0.6378 degrees, respectively. Since the full width at half maximum is inversely proportional to the nanocrystal size (Scherrer equation), this result further confirms the hypothesis that higher hydrothermal temperatures produce greater TiO$_2$ crystallization. The presence of graphene cannot be confirmed in the XRD spectra for the RGO/TiO$_2$ samples because there was no peak in the XRD spectrum that can be attributed to graphene. The most likely explanation is that the relatively weak and broad characteristic peak of graphene at 24.5 degrees was masked by the strong (101) TiO$_2$ reflections at 25.4 degrees.

Transmission electron micrographs of the samples are shown in Figure 3 along with the size distributions of the TiO$_2$ nanoparticles. The nanoparticles were distributed uniformly on the basal plane of RGO nanosheets. The nanoparticles appeared to have a rounder shape in the 180 RGO/TiO$_2$ sample when compared to the 120 RGO/TiO$_2$ sample. The average size of the nanoparticles for the 120 RGO/TiO$_2$, 150 RGO/TiO$_2$, and 180 RGO/TiO$_2$ was $20.4 \pm 3.9$ nm, $20.5 \pm 4.7$ nm, and $21.3 \pm 3.5$ nm, respectively. The histograms of the size distribution of the nanoparticles in the nanocomposites are exhibited on the right hand side of Figure 3. The size distribution of the TiO$_2$ nanoparticles was narrower when the hydrothermal temperature increased. This trend agrees with the observation of more crystallized, round shaped, and homogeneous particles at 180°C compared to the less crystallized, amorphous, and heterogeneous particles at 120°C. The role of TEA in the formation of the nanocrystals can be clearly seen in Figure 4 which shows a transmission electron micrograph of the RGO/TiO$_2$ sample synthesized under the same conditions at 180°C but without the presence of TEA. The TiO$_2$ nanoparticles agglomerated and did not distribute homogenously on the RGO sheet.
Figure 3 (A, C and E) Transmission electron micrograph and (B, D and F) histogram of reduced graphene oxide/titanium oxide nanocomposites at (A and B) 120°C, (C and D) 150°C, and (E and F) 180°C.
The successful decoration of TiO$_2$ nanoparticles on RGO is also reflected in the TGA curves (Figure 5). The TGA curves for all the nanocomposites had four distinct regions (A, B, C, and D). In the region up to 100°C (region A), the sample weight loss was caused by the resorption of physisorbed water. Between 150°C–300°C (region B), the weight loss was a result of the decomposition of labile oxygen-containing functional groups like carboxylate, anhydride, or lactone groups. Region C occurred between 300°C–500°C and was associated with the removal of more stable oxygen groups such as phenol, carbonyl, and quinine. Above 500°C (region D), high temperature pyrolysis of carbon skeleton occurred.$^{50}$ GO displayed a drastic weight loss (40% of its original weight) in region B caused by the decomposition of labile oxygen-containing functional groups such as epoxy and hydroxyl groups. There was a similar loss of weight for the RGO, but the change was not so big. This result indicates that most of the GO oxygen-containing functional groups were reduced during the hydrothermal process, thereby increasing the thermal stability of the RGO.$^{61}$ For the nanocomposites in region B, the percentage of weight loss decreased with hydrothermal temperature. Specifically, the 120 RGO/TiO$_2$, 150 RGO/TiO$_2$, and 180 RGO/TiO$_2$ samples lost 14.1%, 7.9%, and 3.5% of their weight, respectively. This result indicates that the 180 RGO/TiO$_2$ sample had the least amount of labile oxygen-containing functional groups attached to the surface. It also further indicates that a low hydrothermal temperature...
The reduction of mercury(II) ions (Hg\textsuperscript{II}) was almost flat and there were no oxidizing and reducing reactions (Figure 6B). Nucleation occurred at the sites, which resulted in the growth of TiO\textsubscript{2} nanoparticles during the hydrothermal process (Figure 6C). The narrow size distribution of the TiO\textsubscript{2} nanoparticles embedded on the graphene nanosheets may be due to the critical control of the TEA molecules. GO was reduced to graphene due to the simultaneous presence of Ti\textsuperscript{4+}, TEA, and hydrothermal treatment.

Figure 7 displays the electrochemical performance of the samples examined by cyclic voltammetry with a scan rate of 50 mV s\textsuperscript{-1}. The background current behavior for bare GCE in potassium chloride supporting electrolyte containing no mercury ions was almost flat and there were no oxidizing and reducing reactions (Figure 7A). On the other hand, the results for the bare GCE using the potassium chloride electrolyte containing mercury (II) ions (Hg\textsuperscript{II}) in potassium chloride resulted in a distinctive oxidizing peak current observed between +0.1 V and +0.2 V (peak I; Figure 7B). The RGO-modified GCE in potassium chloride supporting electrolyte added with Hg\textsuperscript{II} had an additional reductive peak between –0.2 and +0.2 V (peak II; Figure 7C). The entire hydrothermally prepared RGO/TiO\textsubscript{2}-modified GCE had improved electrochemical performance, signifying an increase in sensitivity to the detection of Hg\textsuperscript{II} (Figure 7D–F). The 150 RGO/TiO\textsubscript{2}-modified GCE exhibited additional oxidation reactions between +0.4 and +1.0 V (peak III) of all the samples. There were two distinct peaks. This oxidation reaction was in addition to the oxidative peak (peak I) seen in the RGO-modified GCE (Figure 7D). The sample also had a trough-like reductive peak (peak II), which shifted to a lower voltage by about 0.2 V, and there was a reductive shoulder between +0.2 and +0.8 V (peak IV). The 180 RGO/TiO\textsubscript{2}-modified GCE showed similar oxidative (peaks I and III) and reductive peaks (peaks II and IV; Figure 7E). For the 120 RGO/TiO\textsubscript{2}-modified GCE, the two reductive peaks (peak II—which shifted by about 0.2 V to the left—and peak IV) were enhanced by approximately 40 μA (Figure 7F) when compared to the 180 RGO/TiO\textsubscript{2}-modified GCE. The peaks most likely arose through the stepwise reduction of Hg\textsuperscript{II} + e\textsuperscript{-} = Hg\textsuperscript{0} and Hg\textsuperscript{2+} + e\textsuperscript{-} = Hg\textsuperscript{0}. The oxidative peak (peak II) that was so pronounced in the 150 RGO/TiO\textsubscript{2} (Figure 7D) and 180 RGO/TiO\textsubscript{2}-modified GCE (Figure 7E) was missing in the 120 RGO/TiO\textsubscript{2}-modified
GCE. Among all the samples, the 120 RGO/TiO$_2$-modified GCE possessed the best reducing reaction, which possibly makes it an efficient redox-recyclable material for the extraction of heavy element ions from wastewater.

**Conclusion**
TiO$_2$ (with particle size of about 20 nm) decorated RGO with high uniformity and were successfully synthesized via a simple hydrothermal process using TEA as the coreducing agent and capping agent. This simplified method has great advantage over other published methods of producing graphene-decorated TiO$_2$ nanoparticles. The method allows control of the particle size distribution through alteration of the hydrothermal temperature. This enables the properties of the nanocomposite to be tailored to a specific application, as demonstrated by the detection of mercury ions in the electrochemical cell where the redox peaks in the cyclic voltammetric depended on the hydrothermal reactor temperature. This synthesis method can be easily extended to the fabrication of other classes of RGO-based nanocomposites. The red-shift phenomenon in the UV analysis demonstrates the applicability of nanocomposites in photovoltaic and photocatalytic applications. The RGO/TiO$_2$ nanocomposites demonstrated enhanced electrochemical performance for the detection of Hg$^{2+}$, suggesting the possibility of using them for detection of the heavy metal.

**Acknowledgments**
This work was financially supported by the High Impact Research Grant (UM.C/625/1/HIR/030) from the University of Malaya, the High Impact Research Grant (UM.C/625/1/HIR/MOHE/05) from the Ministry of Higher Education Malaysia, University of Malaya Research Grant (RG096-10AFR) and the Postgraduate Research Grant (UM.C/241/9) from the University of Malaya. BYS Chang would like to thank The Bright Sparks Unit of University of Malaya for the research incentives.

**Disclosure**
The authors report no conflicts of interest in this work.

**References**


